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Optimization of a Flame Ionization Detector for Determination of Hydrocarbon in Diluted Automotive Exhausts

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THE FLAME IONIZATION DETECTOR has been widely applied to the measurement of total hydrocarbon emission levels of motor vehicles. To obtain accurate analysis of these complex hydrocarbon mixtures, the response of the flame ionization detector (FID) to each carbon atom in the exhaust sample must be the same as to the single hydrocarbon in the calibration gas. Several investigators, however, have determined that the response of the FID to the various exhaust hydrocarbons is not necessarily uniform. (1,2,3)* In particular, the presence of O_2 in the sample can cause the responses of the sample hydrocarbons to differ substantially from that of the calibration gas. It has been suggested that a preflame oxidation of the hydrocarbons at the core of the flame prevents the later ionization that produces the signal.(1) Since the ease of oxidation of hydrocarbons differs for each species, preferential preflame oxidation can give different sensitivities for different hydrocarbons.

Of all the makes and models of FID's currently available for automotive emission testing, the Beckman Model 400 is one of the most common. It is used by the Environmental Protection Agency (EPA) at their Ann Arbor, Michigan facility for vehicle certification and by many other emission test facilities.

Characterization of the Beckman Model 400 hydrocarbon analyzer was originally undertaken to improve instrument-to-instrument correlation. This was later expanded to include an investigation of operating parameters and their effect on relative response characteristics as it became

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* Numbers in parentheses designate References at the end of the paper.

ABSTRACT

The effects of burner flow parameters, fuel type, and fuel composition on the uniformity of relative response of a Flame Ionization Detector (FID) hydrocarbon analyzer were experimentally investigated. Means have been found to improve correlation between analyzers and to optimize relative response characteristics. Although this investigation was directed at analyzers being used for analysis of dilute exhaust sample bags from the Federal Vehicle Emission Test, the results can be applied to a FID in other applications.

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apparent that response characteristics affect not only correlation, but the ultimate accuracy of hydrocarbon measurements.

THEORY

A diagram of the burner of the FID is shown in Figure 1. After being premixed with the sample, a small stream of fuel (typically hydrogen diluted with an inert gas) is burned at the outlet of the jet as it diffuses into the surrounding burner air.

Introduction of a gas sample containing hydrocarbon into a hydrogen diffusion flame increases the concentration of ions within the flame. This increase in ionization is almost directly proportional to the mass flow rate of carbon atoms into the flame. A DC voltage between the burner jet and the collector electrode which surrounds the flame collects the ions, causing current to flow through the associated electronic measuring circuits.

The major mechanism of flame ionization is generally accepted to be: (1)

$$CH + O \longrightarrow CHO^+ + e^- \qquad (1)$$

$$CHO^+ + H_2O \longrightarrow H_3O^+ + CO \qquad (2)$$

$$H_3O^+ + e^- \longrightarrow H_2O + H \qquad (3)$$

CH radicals are produced by thermal cracking of the hydrocarbon molecules in the hydrogen flame. The CHO^+ concentration is highest in the flame reaction zone. Away from the flame its concentration rapidly diminishes by reaction 2 above. The H_3O^+ ions formed are only slowly diminished by reaction 3 above and are, therefore, the most abundant ions outside the actual flame. Oxygen atoms are produced in the reaction zone by the following reversible reactions:

$$H_2 + OH \rightleftharpoons H_2O + H$$

$$H + OH \rightleftharpoons H_2 + O$$

$$H + O_2 \rightleftharpoons OH + O$$

Carbon atoms bonded to hydrogen generally respond linearly with mass flow rate into the burner. Carbon atoms bonded to atoms other than carbon and hydrogen generally have a greatly reduced response. For example, carbon atoms double-bonded to oxygen have essentially zero response.

The rate of ion production for a constant mass flow rate of hydrocarbons into the flame is dependent on fuel and air flow rates. Ion production will peak at definite flow rates of fuel and air. Even when peaked, the FID typically produces and measures only one ion for every 10^5 carbon atoms introduced to the flame. (4)

The above discussion of mechanisms applies to a true diffusion flame. A true diffusion flame results when the only source of oxygen is external oxygen into which hydrogen fuel has diffused. Most chromatographic FID's operate with true diffusion flames due to their use of oxygen-free carrier gases. When a FID is operated as a total hydrocarbon analyzer, any oxygen present in the sample provides an internal source of oxygen within the core of the flame, since it is premixed with the fuel prior to combustion. Because of this internal source of oxygen, the mechanisms of ion formation become much more complex and the response of the FID to different hydrocarbon types becomes non-uniform. This is due to two competing mechanisms that occur in the flame when internal oxygen is present. One mechanism is the preflame oxidation of sample hydrocarbons within the core of the flame which prevents their later ionization. Since some hydrocarbons are oxidized more readily than others, selective oxidation takes place resulting in different sensitivities for different species. A second mechanism is increased oxygen atom formation within the flame which increases the formation rate of CHO^+ ions by means of reaction (1) and, therefore, increases overall FID sensitivity. (1)

TEST EQUIPMENT AND PROCEDURES

ANALYZERS - Four Beckman Model 400 hydrocarbon analyzers were characterized. These hydrocarbon analyzers contain a flame ionization detector; fuel, air, and sample flow regulation systems; electronic amplification circuitry; and a heater and fan to maintain both the electronics and flow regulation systems at a constant temperature (50° C).

Before the analyzers were accepted for use, they were inspected for damage or defective parts and repaired when necessary. The burner configurations were also checked for similarity. All four analyzers were equipped with the short length burner tip (Beckman Part No. 633175) which replaces the longer tip (Part No. 102259).* The analyzers were not equipped with the combustion chamber with the cutback Teflon lip (Part No. 73514) which is the recommended replacement combustion chamber.**

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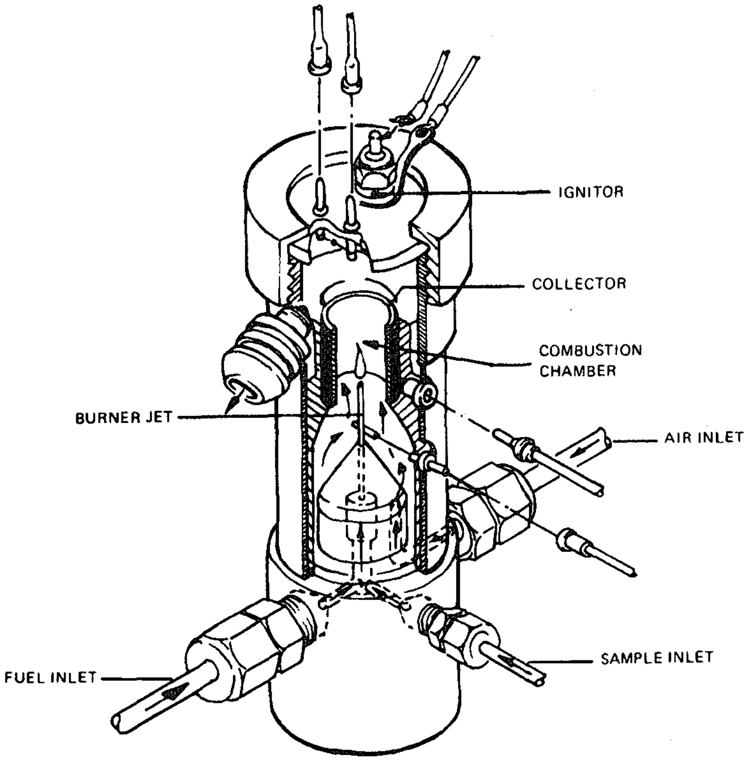
* Beckman Service Memo, January 1972.

** Beckman Service Memo, December 1972.



As pictured in Beckman service manual.

Fig. 1 - Burner assembly of Beckman Model 400 FID

The 100 mv output of the analyzers was monitored by a digital voltmeter and a four-channel strip chart recorder.

SAMPLE SYSTEM - All four analyzers received span, zero, and sample gases from a common stainless steel manifold. From this, the gas flowed through individual flow control valves to each analyzer by way of a 3.5 m length of 0.64 cm diameter Teflon tubing. Each analyzer's internal sample by-pass flow rate was measured at its outlet and maintained at $0.14 m^3/hr$ (5 scfh) by adjustment of the previously mentioned flow control valve.

All test gases from cylinders were introduced into the sample system by braided Teflon lines connected to a quick-disconnect fitting at the entrance of the sample manifold. All samples of dilute vehicle exhaust were contained in Tedlar bags. The exhaust samples were pumped from the bag through a glass fiber filter and into the analyzers by a stainless steel pump.

GASES - Burner air and fuel were supplied to the analyzers using Teflon lines in accordance with the manufacturer's recommendations. Burner air was a synthetic mixture of oxygen (O_2) and nitrogen (N_2) maintained at 20% to 21% O_2* with less than one part per million carbon (ppmC) impurity. The various cylinders of fuel used throughout the study contained H_2 diluted with various amounts of either He or N_2 certified by the supplier to contain less than 5 ppm O_2 and 0.5 ppmC impurity.

The six cylinders of propane/air used to calibrate the analyzers are traceable to the National Bureau of Standards (NBS) propane in air standards. A list of the gases used is shown in Table I. Zero gas was either N_2 or synthetic air. Nitrogen came from the in-house supply of liquid nitrogen. This nitrogen has been periodically monitored and found to contain less than 1 ppmC impurity. Zero air was the same synthetic blend of O_2 and N_2 used for burner air which contained less than 1 ppmC impurity.

Twelve cylinders of individual exhaust hydrocarbons in air were used in this study to measure FID response. Only the methane and the propane cylinders are traceable to NBS standards. Where the actual concentrations were not known and standards were not available for comparison, the cylinders were analyzed using a gas chromatograph, calibrated with propane. In general, the accuracy of the gas chromatograph is good, but because the response of its FID has never been specifically measured with known standards of these same hydrocarbons, the measured concentrations of these cylinders could be slightly in error.

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* All reported concentrations will be on a volume basis unless otherwise noted.

CALIBRATION - Each analyzer was calibrated for 0 to 300 ppmC full scale (FS) on the R x 100 analyzer range using four of the propane/air calibration gases. A new calibration curve was developed for each individual test of burner flow parameters. The calibration curve mid-point was checked before and after each test condition, or at least twice daily. For a test to be validated, the mid-point must have fallen within 0.3% FS (0.9 ppmC) of the calibration curve used. Span and zero were checked both before and after each sample measurement.

TEST RESULTS

INSTRUMENT-TO-INSTRUMENT CORRELATION - One of the more common methods of optimizing FID performance is to peak analyzer response. Peaking is the adjustment of fuel and air pressure settings for maximum signal output. Sample pressure is set at that value required for analyzer sensitivity.

It had been noted in earlier evaluations and during use of the Beckman 400 hydrocarbon analyzer that instrument-to-instrument correlation was poor when measuring either test gases containing various individual hydrocarbons or dilute exhaust bags from the Federal Emission Test. From an investigation into these correlation difficulties, it was discovered that analyzers that were individually peaked with a common sample pressure had somewhat different flow rates to the FID burner.

Table I - Calibration and Test Gases From Cylinders

Calibration Gases

Gases	Concentration		Referred to in Text as:
	Hydrocarbon (ppmC)	Oxygen (%)	
Propane/Air	73.2	20.1	1C
Propane/Air	123.6	22.5	2C
Propane/Air	125.4	-	3C
Propane/Air	158.4	20.9	4C
Propane/Air	249.3	-	5C
Propane/Air	250.8	20.9	6C

Test Gases

Gases	Hydrocarbon (ppmC)	Oxygen (%)	Referred to in Text as:
Methane/Air	183.0	21.2	1T
Ethane/Air	173.7	20.8	2T
Propane/Air	174.3	16.5	3T
Ethylene/Air	164.4	18.6	4T
Propylene/Air	169.5	17.7	5T
Benzene/Air	172.8	20.9	6T
Toluene/Air	159.0	20.9	7T
Acetylene/Air	159.6	18.0	8T
Methane/N_2	208.5	0.0	9T
Propane/N_2	155.4	0.0	10T
Ethylene/N_2	169.2	0.0	11T
Propylene/N_2	151.5	0.0	12T

To determine if instrument-to-instrument correlation was improved by the setting of equal flow rates to the burner, the variation in measurements of four analyzers was determined using both test gases from cylinders and dilute exhaust. The test gases were blends of air or nitrogen containing various individual hydrocarbons also found in exhaust, and the exhaust samples were dilute exhaust bags of Federal Emission Tests of both 1974 and 1975 vehicles. After the variations in measurements were recorded with all four analyzers peaked, the test was repeated with the analyzers set at similar conditions, but with equal burner flow rates. Equal flow rates were set by developing curves of flow rate versus pressure for the fuel, air, and sample restrictors; and then setting the pressures to achieve the desired flow rates. A set of typical flow curves is shown in Figure 2. A rough average of the peaked flow rates was used for the final settings. They were: sample, 15 cc/min; fuel, 100 cc/min; and air, 400 cc/min.

Some improvement was found in instrument-to-instrument variation by setting equivalent burner flow rates rather than peaking each analyzer. The root mean square standard deviation of the measurements of ten different hydrocarbons was reduced from 1.1 ppm measured as propane (ppmp) to 0.5 ppmp, which was statistically less at the 95% confidence level. The relative standard deviation of dilute exhaust bag measurements was reduced for a majority of exhaust sample types, although there was insufficient data to prove that this reduction was statistically significant at the 95% confidence level. Individual analyzer measurements are listed in Table II.

As a result of this correlation study, it became apparent that two analyzers with different flow parameters can measure various hydrocarbons and dilute exhaust bags differently, although they both measure the propane span gas alike. Because of this, it was decided to further investigate and attempt to characterize the effect of burner flow parameters on the total hydrocarbon measurements of the Beckman Model 400 FID and determine those combinations of burner flow parameters which result in accurate measurement of total hydrocarbons.

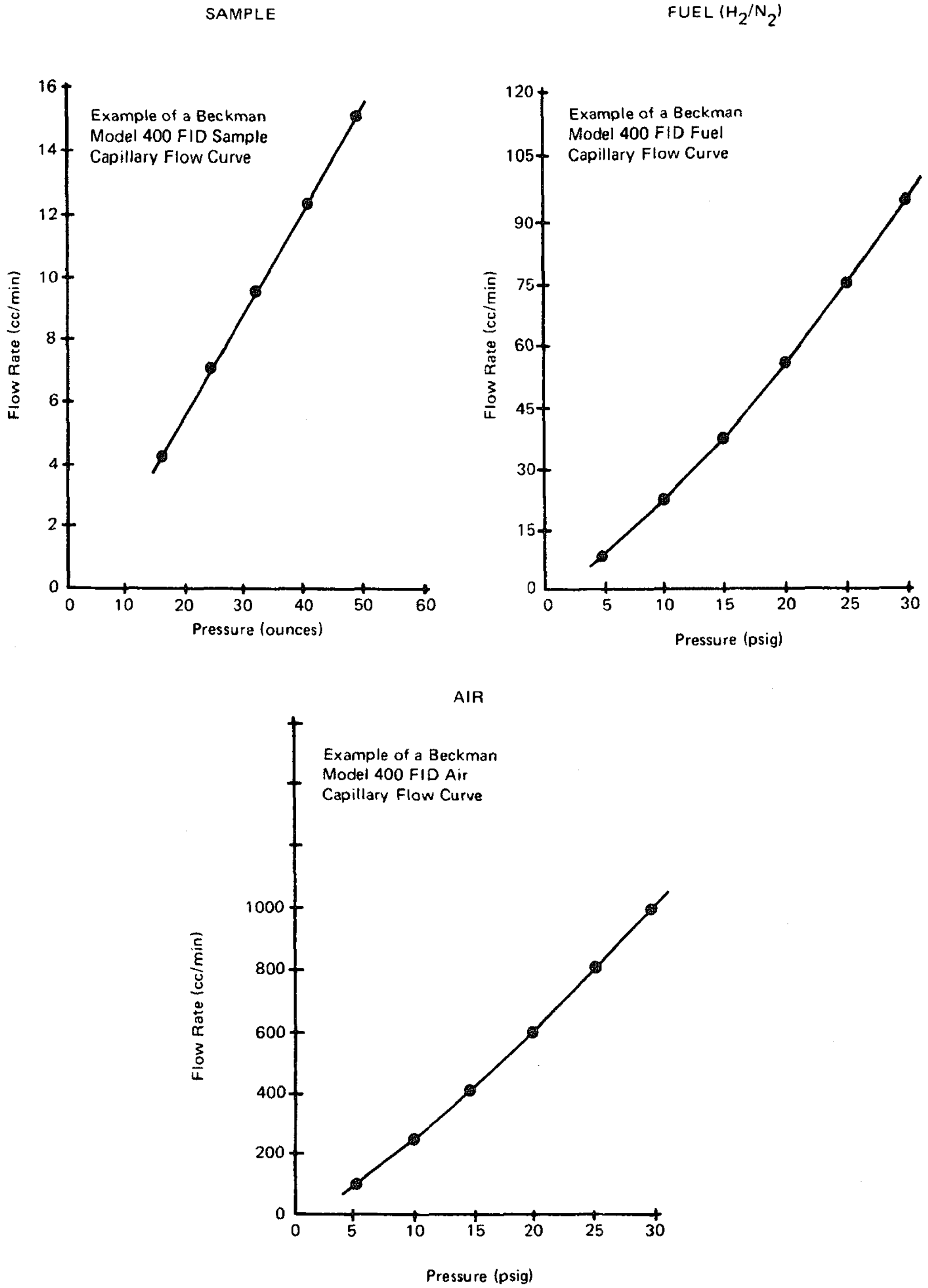

Fig. 2 - Example of pressure versus burner flow rate curves for Beckman Model 400 Analyzers

RELATIVE RESPONSE CHARACTERISTICS -

To obtain accurate analysis of complex hydrocarbon mixtures, it is necessary to have the response of the FID to each carbon atom in the sample equal to the response of the FID to each carbon atom of the single hydrocarbon calibration gas. Therefore, to evaluate the effects of burner flow parameters, fuel type, and fuel composition on FID accuracy, it is necessary to examine their effect on the relative response characteristics of the FID.

Burner Flow Rate Parameters - The change in relative response of some typical exhaust hydrocarbons was measured as a function of various sample, fuel, and air flow rates to the burner. Relative response was measured as the apparent analyzer reading divided by the actual concentration of the sample. For example, if a sample measured 10% higher than its actual concentration, its relative response was 1.10. Since the analyzers were calibrated with propane/air

Table II - Instrument-To-Instrument Correlation

Cylinder Gases

		Optimized by Peaking					Optimized by Setting Equal Flow Rates				
		Analyzer Measurements (ppmp)					Analyzer Measurements (ppmp)				
No.	**Gas**	B-1	B-2	B-3	B-4	Standard Deviation	B-1	B-2	B-3	B-4	Standard Deviation
1T	Methane/Air	70.6	73.5	70.5	72.9	1.5	73.4	73.0	73.1	72.6	0.3
3T	Propane/Air	59.8	59.6	59.6	59.8	0.1	59.7	59.7	59.7	59.7	0.0
4T	Ethylene/Air	51.6	49.6	51.7	50.1	1.1	50.0	49.8	50.0	50.4	0.3
5T	Propylene/Air	52.0	49.1	51.8	50.1	1.4	49.6	49.2	49.5	50.3	0.5
7T	Toluene/Air	44.6	44.7	43.0	44.8	0.9	41.3	41.2	40.5	42.3	0.7
8T	Acetylene/Air	62.0	64.0	62.9	61.5	1.1	63.4	62.3	64.0	61.9	1.0
9T	Methane/N_2	79.2	81.1	78.9	80.4	1.0	80.8	80.9	80.6	80.5	0.2
10T	Propane/N_2	58.4	59.4	56.4	59.8	1.5	59.4	59.5	59.1	59.7	0.3
11T	Ethylene/N_2	62.4	62.9	61.8	63.4	0.7	62.9	63.0	62.5	63.4	0.4
12T	Propylene/N_2	56.8	56.8	56.0	57.5	0.6	57.0	56.9	56.5	57.5	0.4
Root Mean Square Standard Deviation						1.07					0.48

Dilute Exhaust Bags

			Optimized by Peaking			
			Analyzer Measurements (ppmp)			
Car	Type Test	Bag	B-1	B-2	B-3	B-4
1	74	1	37.1	37.7	38.0	38.7
2	74	1	61.9	62.4	63.0	63.4
3	74	1	56.6	57.5	58.1	58.9
4	75	1	50.4	49.9	49.6	50.8
		2	3.0	3.1	3.0	3.5
		3	9.1	9.1	8.5	9.1
5	75	1	41.0	40.6	40.3	41.1
		2	6.1	5.1	4.4	4.7
		3	14.9	15.0	14.6	15.2
6	75	1	45.6	46.5	46.4	48.0
		2	4.3	3.6	3.0	3.1
		3	6.6	6.2	5.8	5.8
7	75	1	59.8	60.3	60.7	61.9
		2	16.8	18.2	17.1	17.9
		3	35.2	35.5	35.2	36.1
8	75	1	52.2	52.5	52.5	54.4
		2	24.3	25.8	24.9	26.1
		3	52.9	53.6	53.7	55.2
9	Steady State	10 mph	8.0	8.1	7.9	8.2
		60 mph	17.6	18.2	16.9	17.1
10	Steady State	40 mph	13.9	14.5	13.2	14.2
		60 mph	58.2	59.4	59.8	61.3

			Optimized by Setting Equal Flow Rates			
			Analyzer Measurements (ppmp)			
Car	Type Test	Bag	B-1	B-2	B-3	B-4
11	74	1	48.1	48.2	48.0	48.5
12	74	1	66.3	66.8	66.3	67.1
13	74	1	51.9	52.1	51.8	52.8
14	74	1	36.9	37.0	36.7	37.5
15	75	1	33.6	34.0	32.7	34.3
		2	8.6	9.1	9.0	9.6
		3	15.3	15.6	15.1	15.7
16	75	1	69.0	69.3	69.4	69.5
		2	4.0	4.1	4.0	4.2
		3	12.2	12.4	12.4	12.7
17	75	1	49.2	49.4	48.9	49.8
		2	4.0	4.4	4.3	4.7
		3	8.2	8.1	8.3	8.3
18	75	1	37.3	37.8	37.7	38.4
		2	8.2	8.4	8.5	8.6
		3	19.5	19.8	19.4	20.1
19	Steady State	20 mph	3.0	3.0	2.7	2.7
20	Steady State	40 mph	8.5	8.5	8.6	8.6

Summary - Dilute Exhaust Bags

Type Test	Bag	No. of Bags	Mean Reading	Standard Deviation of the Means	Percent Relative Standard Deviation	No. of Bags	Mean Reading	Standard Deviation of the Means	Percent Relative Standard Deviation	Is the variance of "Flow Setting" statistically less than "Peaking" at 95% confidence level? *
74	1	3	52.8	0.76	1.4	4	51.0	0.34	0.7	No
75	1	5	50.2	0.68	1.4	4	47.5	0.38	0.8	No
	2	5	10.9	0.30	2.7	4	6.5	0.24	3.7	No
	3	5	23.9	0.31	1.3	4	13.9	0.19	4.1	No
Steady State		4	24.8	0.40	1.6	2	5.7	0.06	1.0	No

* Using the F test for homogeneity of variance.

mixtures at each set of flow parameters, the measured responses are all relative to propane. Therefore, it should be kept in mind that propane, although a straight line on the accompanying graphs, may be more sensitive to the parameters being changed than are other gases.

For the study of relative response, burner fuel was 43% H_2/N_2 which approximates the 40% H_2/N_2 fuel used by many facilities for the Beckman 400 analyzer and other FID analyzers. The effect of sample, fuel, and air flow parameters on relative response is shown in Figures 3 through 5.

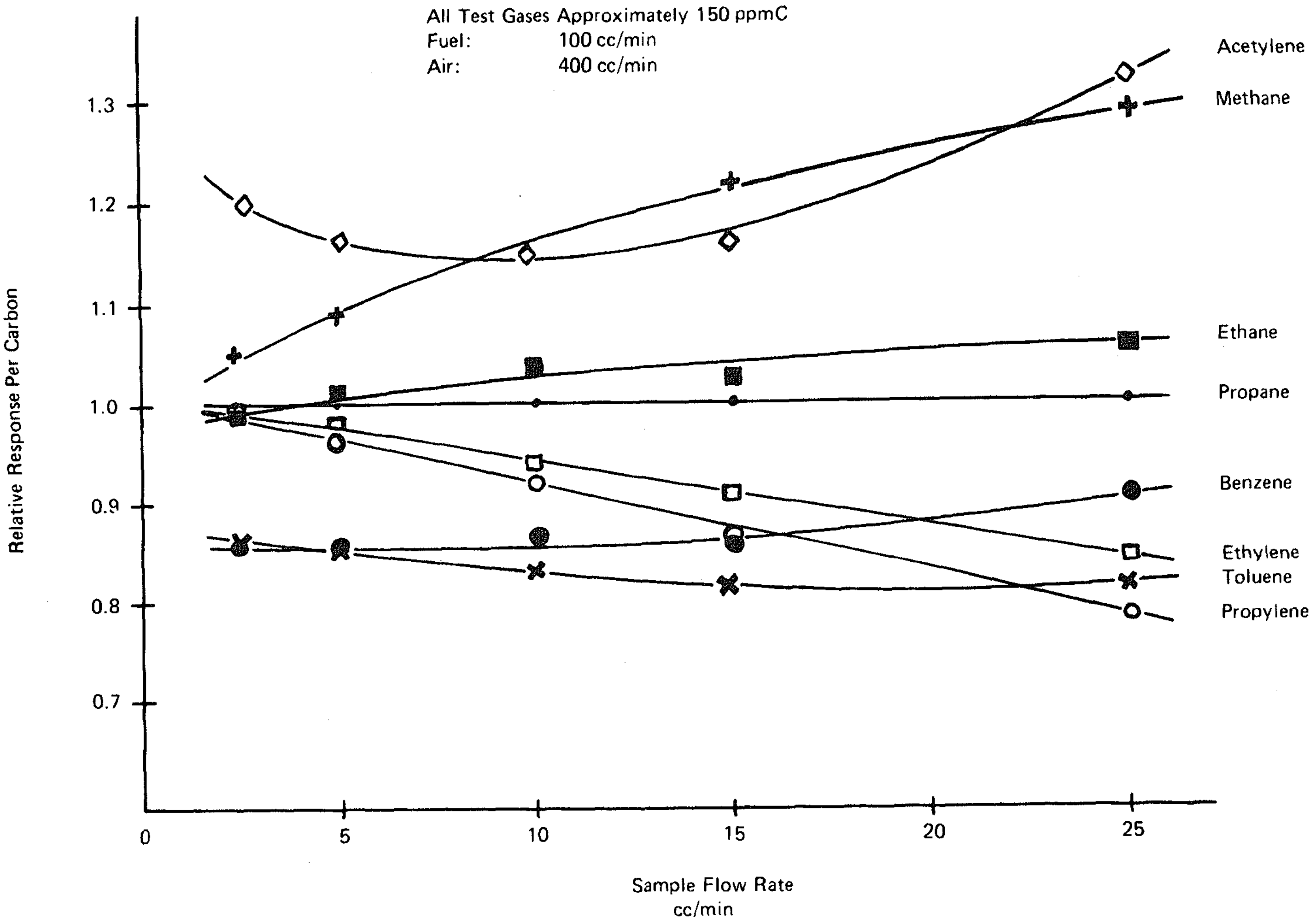

Fig. 3 - Effect of sample flow rate on relative response - fuel type: H_2/N_2

At high sample flow rates, the relative response to the various hydrocarbons tested is significantly non-uniform (Figure 3). As sample flow rate is decreased, the relative response of the paraffins (methane and ethane) and the olefins (ethylene and propylene) tends to converge to 1.0. The aromatics (benzene and toluene) are relatively insensitive to sample flow rate and never obtain a relative response above 0.9. Acetylene, which has been reported to follow a different ionization mechanism, (1) reaches a minimum relative response of 1.15 at 10 cc/min sample flow rate; in general its relative response remains quite high.

The Beckman Model 400 FID, when operated with H_2/N_2 fuel, typically consumes between 60 and 100 cc/min of fuel which corresponds to roughly 20 to 30 psig fuel pressure. Within this range, more uniform response was found at the higher fuel flow rates (Figure 4). Relative response was much less sensitive to fuel flow rate at low sample flow rates than it was at high sample flow rates.

Quite a significant loss of total analyzer sensitivity occurred when air flow rate was reduced below approximately 250 cc/min. Above this, air flow rate had only a slight effect on sensitivity and little or no effect on the relative response of the hydrocarbons tested, with the exception of acetylene.

The above study of various sample, fuel, and air flow rates was repeated with 40% H_2/He substituted for the H_2/N_2 fuel used previously. The effects of sample and fuel flow rate parameters on relative response is shown in Figures 6 and 7. The effect of air flow rate parameters were found to be very similar to those found for H_2/N_2 fuel with little or no effects above 250 cc/min, and therefore, is not shown.

At high sample flow rates, the relative response of the various hydrocarbons tested was again significantly non-uniform (Figure 6). As sample flow was decreased, the relative response to the paraffins and the olefins converged toward

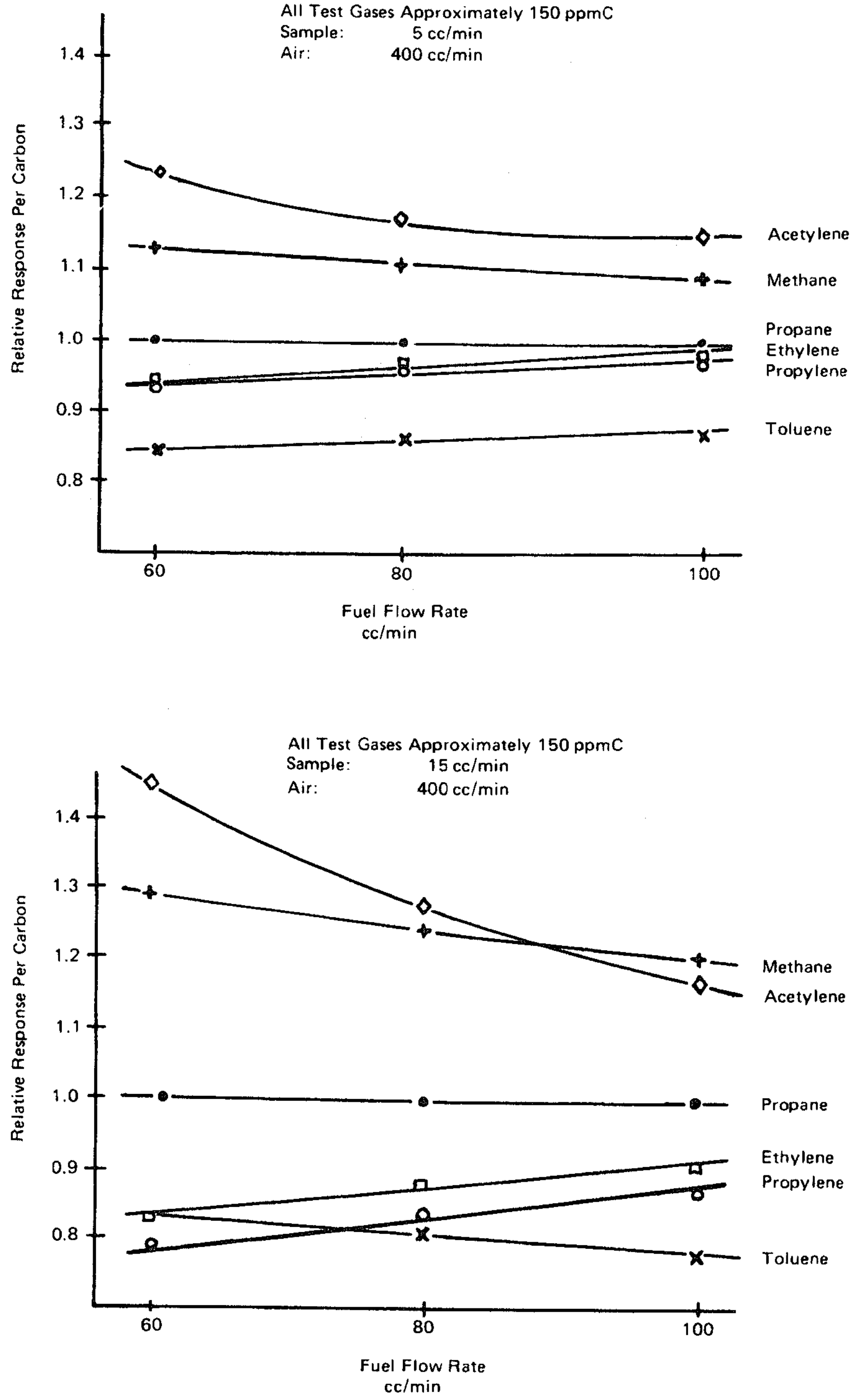

Fig. 4 - Effect of fuel flow rate on relative response - fuel type: H_2/N_2

1.0. The aromatics were nearly insensitive to sample flow rate and remained at a relative response between 0.89 and 0.93. The relative response to acetylene remained high, with a minimum value of 1.20 at 5 cc/min sample flow.

The Beckman Model 400 FID, when operated with H_2/He fuel, typically consumes between 70 and 120 cc/min of fuel which corresponds to roughly 20 to 30 psig fuel gauge pressure. Within this range of fuel flow rates, more uniform relative response was found at the higher fuel flow rates (Figure 7). However, relative response was much less sensitive to fuel flow rate at low sample flow rates than it was at high sample flow rates.

Comparison of relative response between the two fuel types at similar flow parameters is shown

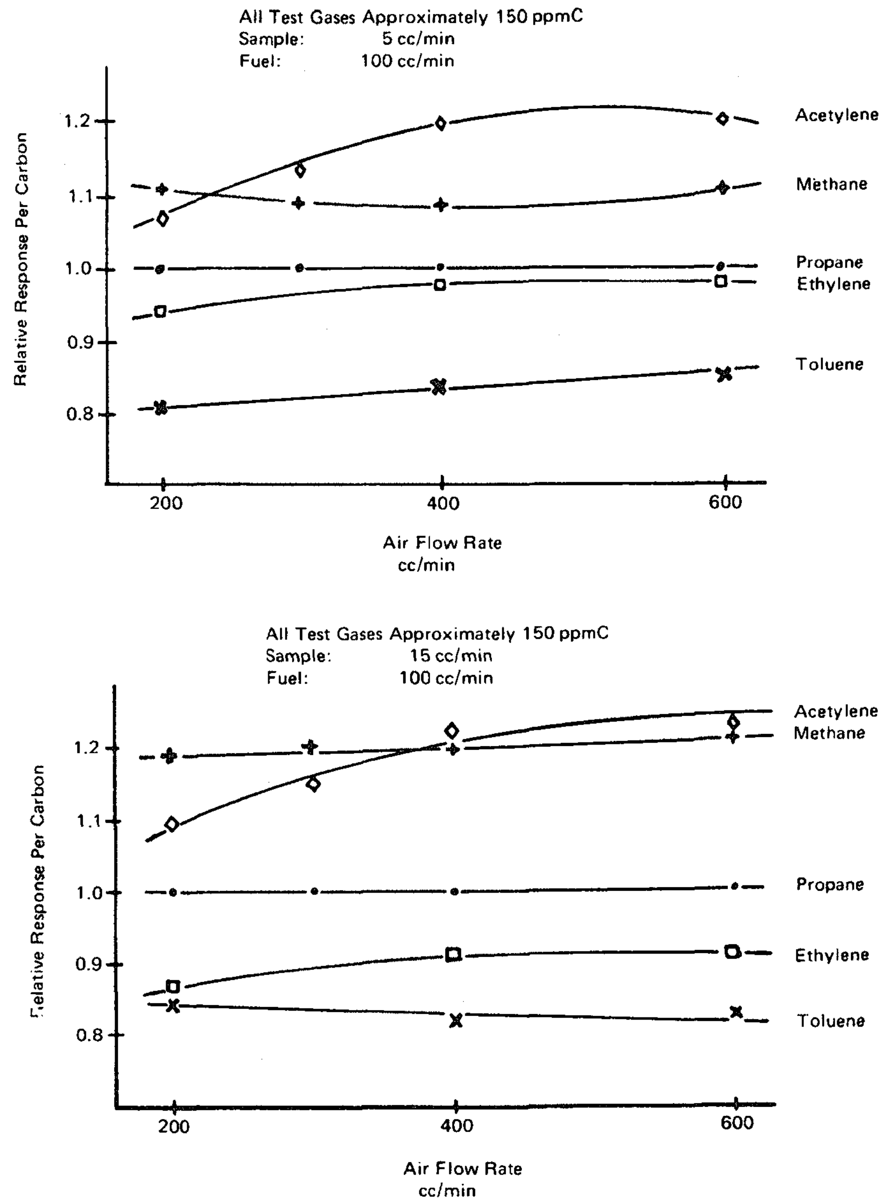

Fig. 5 - Effect of air flow rate on relative response - fuel type: H_2/N_2

in Figures 8 and 9. At any one set of flow parameters, H_2/He fuel gave slightly more uniform relative response to the hydrocarbons tested than did the H_2/N_2 fuel. However, the overall effects of sample or fuel flow rate changes on relative response are very similar for the two fuels. Note that the relative response to the aromatics, which was somewhat insensitive to burner flow parameters, is sensitive to fuel type; relative response being close to 1.0 with the use of H_2/He fuel.

Dilute Exhaust - Four Beckman analyzers were connected in parallel to simultaneously measure the hydrocarbon content of dilute exhaust bags from the 1975 Federal Emission Test. To determine the effect on bag measurements of low versus high sample flow rate, two of the analyzers were set at 5 cc/min and the remaining two analyzers at 25 cc/min. Fuel (H_2/N_2) and air flow rates were maintained at 100 cc/min and 400 cc/min respectively for all four analyzers. Dilute exhaust bags from six 1975 catalyst vehicles were measured by all four analyzers. After the bags from three of the vehicles were measured, the sample flow rates of the analyzers were interchanged to reduce the effect of any geometric differences between analyzers. The individual bag measurements, along with the mass emissions calculated from those measurements are listed in Table III.

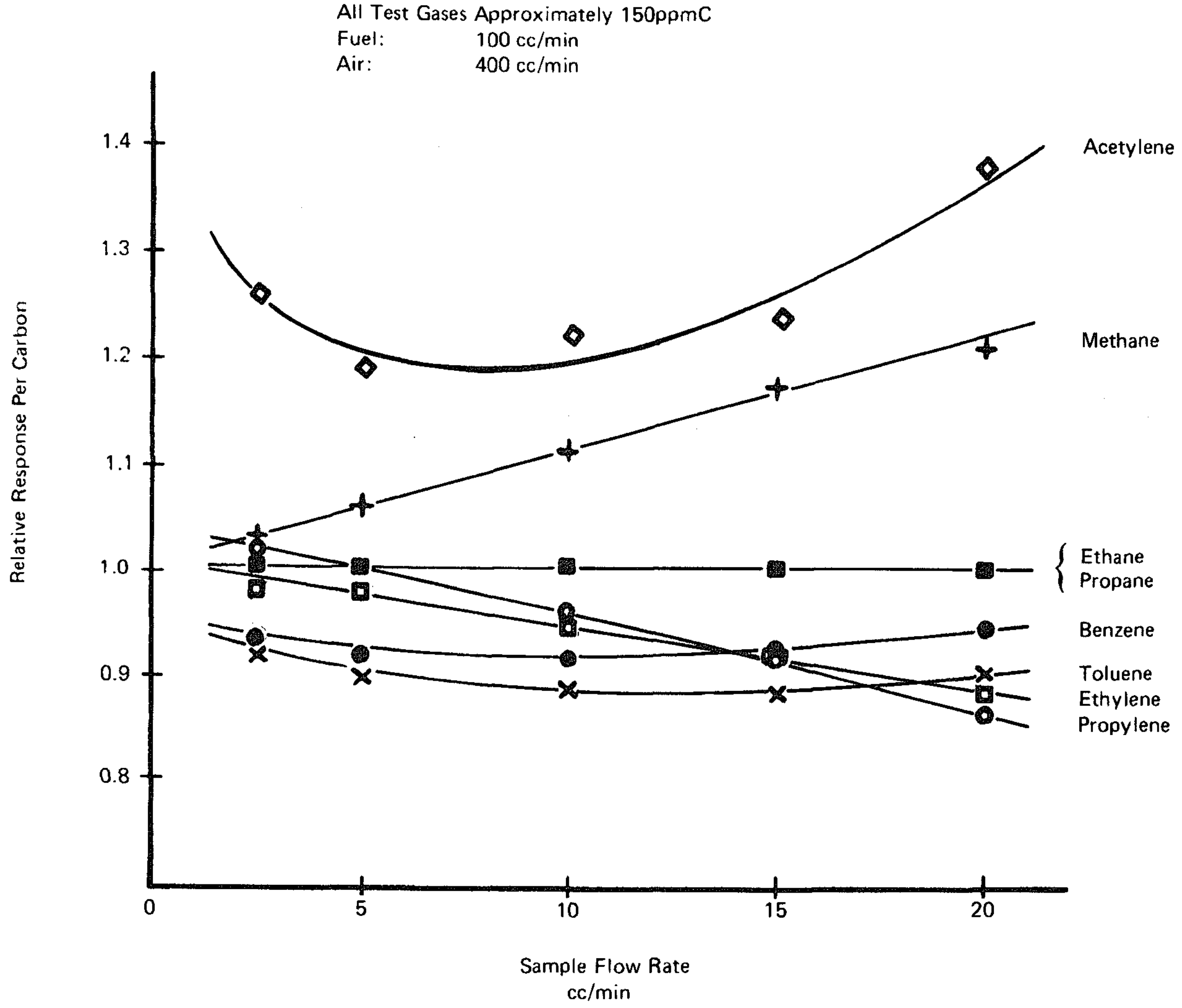

Fig. 6 - Effect of sample flow rate on relative response - fuel type: H_2/He

A sample flow rate of 5 cc/min gave 5% to 7% higher measurements, on the average, than a sample flow rate of 25 cc/min, with individual bag measurements ranging from 3% lower to 30% higher. The calculated mass emissions from the measurements made by analyzers with the low sample flow rate, which had the more uniform response characteristics, averaged approximately 7% higher than those calculated from the measurements of analyzers with the high sample flow rate.

To further determine the effects of fuel type and sample flow rate on hydrocarbon emission measurements, four analyzers were set up as follows:

Analyzer Number	B-3	B-1	B-4	B-2
Fuel diluent	N_2	He	N_2	He
Fuel flow rate (cc/min)	75	90	75	75
Sample flow rate (cc/min)	2.5	2.5	16	16
Air flow rate (cc/min)	335	380	270	270

Nine 1975 cold start emission tests were performed on nine 1975 vehicles, each with approximately 4,000 accumulated vehicle miles. As soon as the measurements at the test site were completed, the contents of each dilute exhaust bag were pumped into a second bag and carried to the four analyzers described above for measurement. The bag sample was never allowed to age more than one-half hour before completion of the four hydrocarbon analyzer measurements.

From the individual bag measurements of hydrocarbon content, the resulting hydrocarbon emissions, in g/mi, were computed for each analyzer. Because background bags were not measured by the four analyzers, the test site measurements of the background bags were used in the computations.

The following summarizes the comparison of measured emissions at the four FID settings.

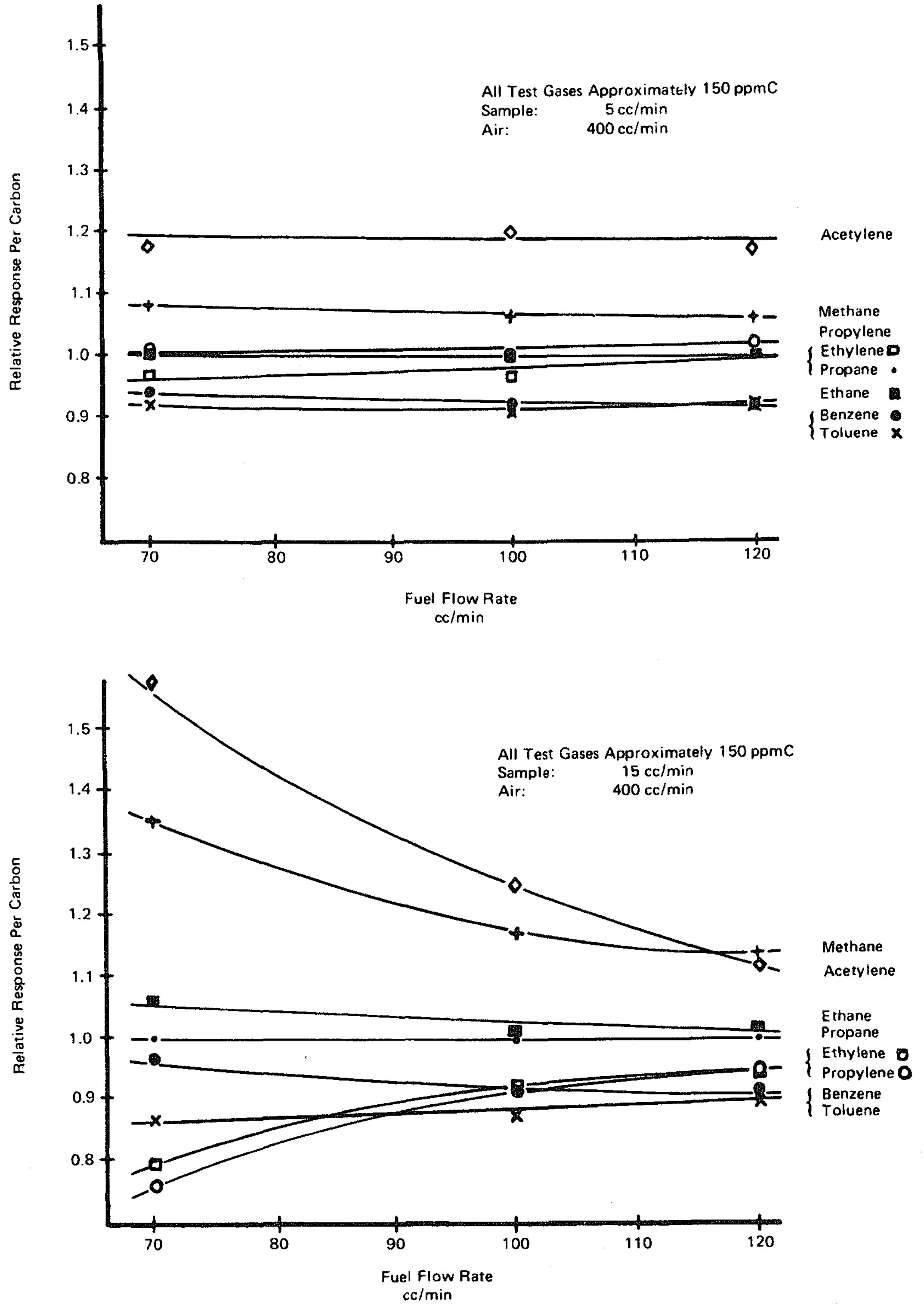

Fig. 7 - Effect of fuel flow rate on relative response - fuel type: H_2/He

Individual analyzer measurements are listed in Table IV.

	Flow Rates & Fuel Type		Mean Percent Difference*	Range of Percent Difference	95% Confidence Interval of Mean Percent Difference
	A	B			
Sample: Fuel:	Low H_2/He	Low H_2/N_2	5.3	2.8 to 10.3	3.5 to 7.1
Sample: Fuel:	High H_2/He	High H_2/N_2	6.7	4.3 to 8.9	5.6 to 7.8
Sample: Fuel:	Low H_2/N_2	High H_2/N_2	6.6	3.4 to 10.3	5.2 to 8.0
Sample: Fuel:	Low H_2/He	High H_2/He	5.3	1.1 to 10.3	3.2 to 7.4

*Percent difference in weighted g/mi emission = $\frac{A - B}{B}$ x 100.

The use of low sample flow rates and/or H_2/He fuel resulted in higher measured emission levels. A high sample flow rate and H_2/N_2 fuel gave approximately 12% lower measurements than a low sample flow rate and H_2/He fuel. In general, when uniformity of response was improved by reduced sample flow rate or the use of H_2/He fuel, higher total hydrocarbon measurements were obtained.

Fuel Composition - Three types of burner fuel for a FID are generally used throughout the industry: pure H_2, 40% H_2/N_2, and 40% H_2/He. Several investigators have recommended the use of mixed fuels (H_2/N_2 or H_2/He) because they have shown that they reduce the sensitivity of the FID to varying O_2 concentration of the sample. (1,3) These same investigators report that, of the two fuels, H_2/He is more efficient in reducing this O_2 effect.

Currently, a vast majority of the automotive emission test facilities are using one or the other mixed fuel for their hydrocarbon analyzers. In some applications of these analyzers, the sensitivity to O_2 concentration may not be of major importance because the O_2 concentration remains relatively constant as it does in dilute exhaust bags from the Federal Emission Test. In these applications, errors due to non-uniform relative response are possibly more significant than the errors due to O_2 effects. Therefore, both fuel type and fuel composition (%H_2) should be optimized with consideration for both relative response characteristics and O_2 effects.

Test Gases from Cylinders - As discussed previously, 40% H_2/He fuel resulted in more uniform relative response than did 40% H_2/N_2 fuel at the same burner flow parameters. The uniformity of relative response of some typical exhaust hydrocarbons was measured with several fuel compositions other than 40% H_2 with both He and N_2 fuel diluents to determine the optimum fuel composition for uniform relative response. Fuel and air flow rates were maintained at 100 and 400 cc/min respectively for every test. Uniformity of relative response for both fuel types was determined at two different sample flow rates. Results are shown in Figures 10 and 11.

In general, uniformity of relative response improved as the concentration of H_2 in the fuel was increased, with either He or N_2 fuel diluent, up to approximately 60% H_2. As H_2 in the fuel was reduced to near the point of flame-out (approximately 35%), divergence from a relative response of 1.0 became quite significant. At 100% H_2, uniformity of relative response was slightly worse than at 60% H_2. With 100% H_2 fuel, sample flow rate could not be reduced below 15 cc/min because the analyzer background became extremely high and unstable, probably due to the burner tip becoming hot enough to emit ions. Fuel composition had a much greater effect on response at high sample flow rates than it did at low sample flow rates.

Dilute Exhaust - To determine the effect of fuel composition on the dilute exhaust bag measurements from the Federal Emission Test, three analyzers were set up, each using fuel of a different composition. The test fuels were 40% H_2/He, 60% H_2/He, and pure H_2. Sample, fuel, and air flow rates were maintained at 15, 100 and 400 cc/min. respectively.

Dilute exhaust sample bags from the 1975 cold start emission tests of eight 1975 catalyst vehicles were measured by these three analyzers and emission levels in g/mi were calculated from the individual measurements. The following summarizes the comparison of measured emission levels of the three FID fuels. Individual analyzer measurements are listed in Table V.

Comparison (A to B)	Mean Percent Difference*	Range of Percent Difference	95% Confidence Interval of Mean Percent Difference
40% H_2/He to 60% H_2/He	-3.9	-7.7% to +2.4%	-7.1% to -0.7%
40% H_2/He to 100% H_2	-4.3	-11.3% to +4.7%	-8.9% to +0.3%

* Percent difference in weighted g/mi emission = $\frac{B - A}{A}$ x 100

An increased hydrogen concentration of the fuel slightly reduced the measured emission level. From the previous data presented, improved uniformity of response increased the measured emission levels. Because the use of 60% H_2/He fuel improved the response characteristics, the

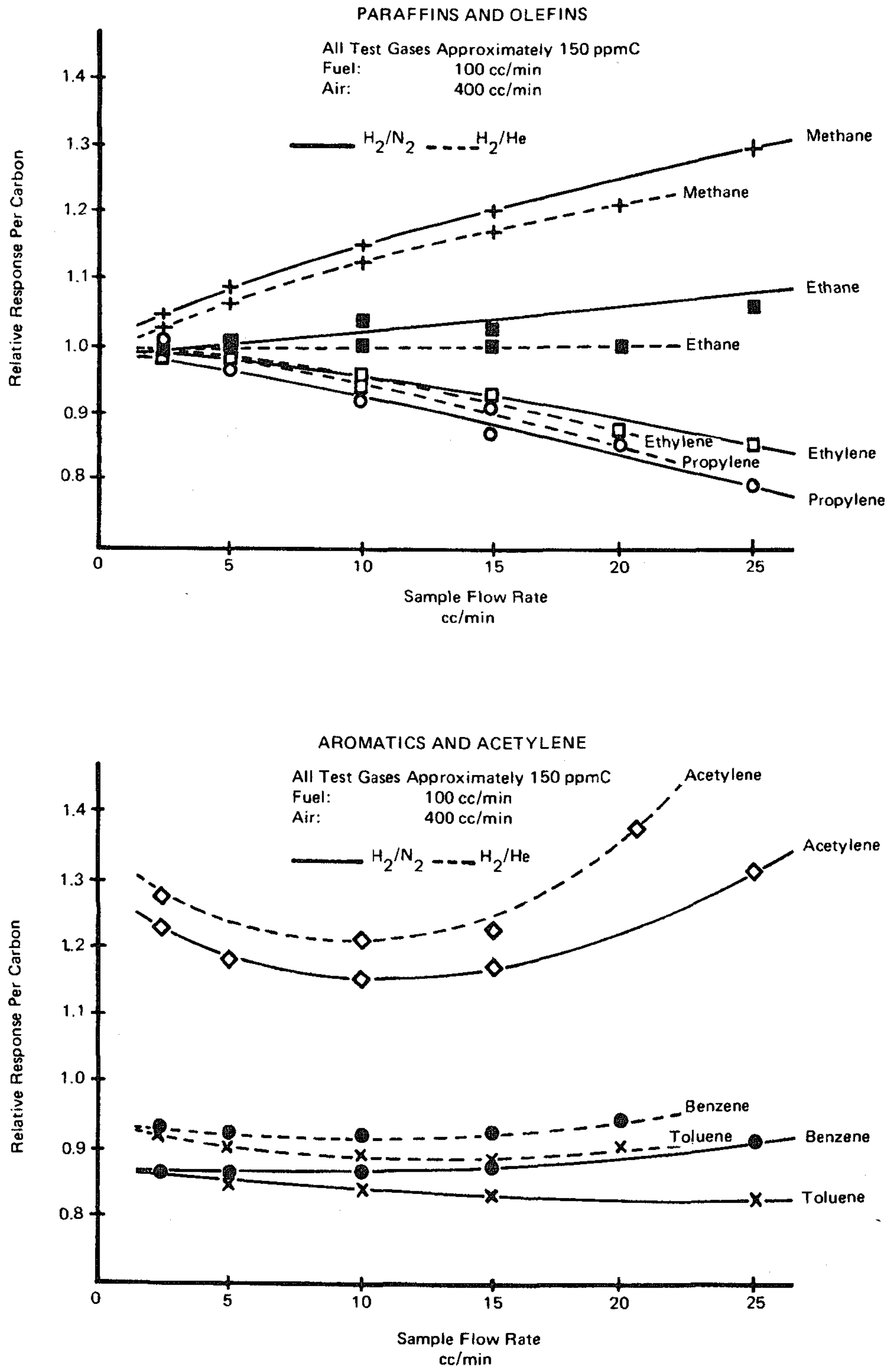

Fig. 8 - Effect of fuel flow rate on relative response - comparison of H_2/N_2 and H_2/He fuel

measured emission levels would be expected to increase, not decrease. This discrepancy could be due to the use of different vehicles or possibly an increased sensitivity to background O_2 concentration. Dilute exhaust bags are typically around 18% O_2 as compared to the 20% - 21% O_2 propane/air span gas.

To test for increased sensitivity to background O_2 concentration, a cylinder of 16.5% O_2 propane/air was measured with the FID's using

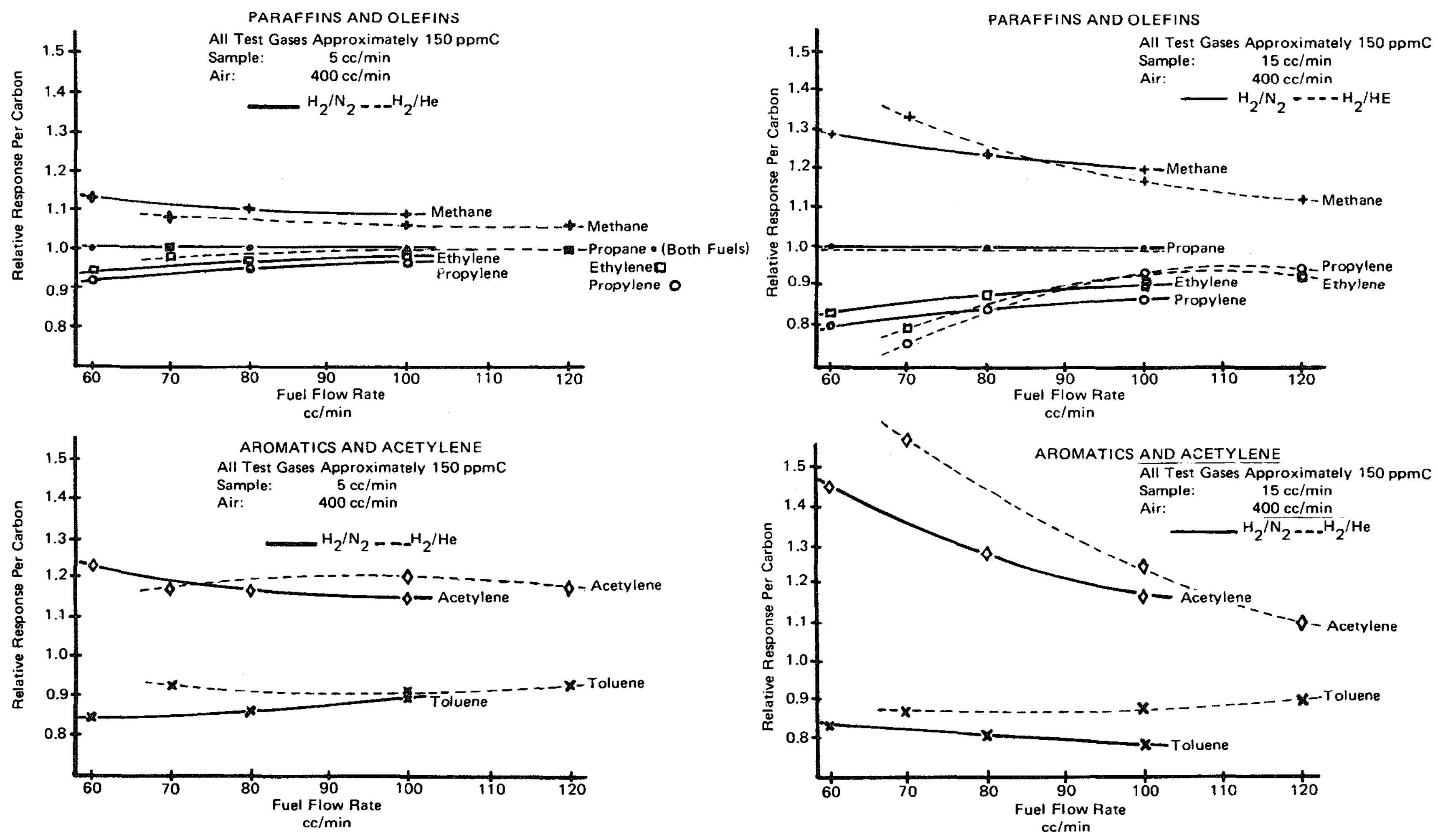

Fig. 9 - Effect of fuel flow rate on relative response - comparison of H_2/N_2 and H_2/He fuel

Table III - Effect of Sample Flow Rate on Dilute Exhaust Bag Measurement

Analyzer:	Beckman Model 400
Fuel Type:	H_2/N_2
Fuel Flow Rate:	100 cc/min
Air Flow Rate:	400 cc/min

			Analyzer Measurements (ppmp)				
			25 cc/min Sample Flow Rate		5 cc/min Sample Flow Rate		
Car	Type	Phase	Analyzer B-1	Analyzer B-2	Analyzer B-3	Analyzer B-4	Percent Difference*
1	75	1	38.7	39.4	39.7	41.0	3.3
		2	18.5	19.5	19.2	20.2	3.7
		3	25.8	26.8	27.2	28.1	5.1
		Weighted g/mi	1.035	1.079	1.076	1.124	4.1
2	75	1	42.3	42.4	44.0	45.0	5.1
		2	11.3	10.6	10.8	10.9	- 0.9
		3	22.3	22.6	22.8	23.3	2.7
		Weighted g/mi	0.811	0.793	0.813	0.828	2.3
3	75	1	34.0	34.3	35.0	36.1	4.1
		2	9.0	8.5	8.3	8.7	- 2.9
		3	16.0	15.8	16.1	16.6	2.8
		Weighted g/mi	0.622	0.607	0.609	0.633	1.1
			B-3	B-4	B-1	B-2	
4	75	1	37.2	38.5	39.7	40.1	5.4
		2	24.8	26.2	26.9	27.0	5.7
		3	38.7	40.4	41.9	42.1	6.2
		Weighted g/mi	1.337	1.404	1.448	1.456	6.0
5	75	1	17.3	18.3	19.0	19.1	7.0
		2	2.8	2.9	3.7	3.7	29.8
		3	4.9	5.0	5.6	5.6	13.1
		Weighted g/mi	0.209	0.220	0.255	0.255	18.9
6	75	1	56.0	57.6	60.9	60.8	7.1
		2	18.9	20.4	21.4	21.4	8.9
		3	30.4	31.8	32.8	33.0	5.8
		Weighted g/mi	1.215	1.285	1.349	1.350	8.0

Average, Range, and Confidence Interval of Percent Difference

Phase	Mean (%)	Range (%)	95% Confidence Interval of Mean % Difference
1	5.3	3.3 to 7.1	4.2 to 6.4
2	7.4	-2.9 to 29.8	-1.4 to 16.2
3	5.9	2.7 to 13.1	3.0 to 8.8
Weighted	6.8	1.2 to 18.9	2.0 to 11.6

$$* \text{ Percent Difference} = \frac{\text{Average 5 cc/min Measurements} - \text{Average 25 cc/min Reading}}{\text{Average 25 cc/min Measurements}} \times 100$$

Table IV - Effect of Fuel Type and Sample Flow Rate on the Measurements of Dilute Exhaust Bags

Analyzer		B3	B1	B4	B2	Percent Difference			
						$\frac{(B1) - (B3)}{B3}$ x 100	$\frac{(B2) - (B4)}{B4}$ x 100	$\frac{(B3) - (B4)}{B4}$ x 100	$\frac{(B1) - (B2)}{B2}$ x 100
Fuel		H_2/N_2	H_2/He	H_2/N_2	H_2/He	Change from H_2/N_2 to H_2/He at 2.5 cc/min Sample Flow Rate	Change from H_2/N_2 to H_2/He at 16 cc/min Sample Flow Rate	Change from 16 cc/min to 2.5 cc/min Sample Flow Rate using H_2/N_2	Change from 16 cc/min to 2.5 cc/min Sample Flow Rate using H_2/He
Fuel Flow Rate (cc/min)		75	90	75	75				
Sample Flow Rate (cc/min)		2.5	2.5	16	16				
Air Flow Rate (cc/min)		335	380	270	270				
Vehicle	Phase	Analyzer Measurement (ppmp)							
1	1	39.0	38.9	36.5	37.7	-0.3	3.3	6.8	3.2
	2	3.9	4.2	3.4	4.0	7.7	17.6	14.7	5.0
	3	6.2	6.6	5.8	6.3	6.5	8.6	6.9	4.8
	Weighted g/mi	0.395	0.407	0.358	0.390	3.0	8.9	10.3	4.4
2	1	47.1	47.5	44.3	45.6	0.8	2.9	6.3	4.2
	2	5.3	5.7	5.2	5.6	7.5	7.7	1.9	1.8
	3	13.1	13.5	12.8	13.2	3.1	3.1	2.3	2.3
	Weighted g/mi	0.576	0.592	0.543	0.573	2.8	5.5	6.1	3.3
3	1	38.3	39.2	35.9	36.9	2.3	2.8	6.7	6.2
	2	4.5	5.2	4.2	4.6	15.6	9.5	7.1	13.0
	3	7.6	7.8	7.3	7.8	2.6	6.8	4.1	0.0
	Weighted g/mi	0.433	0.461	0.404	0.428	6.5	5.9	7.2	7.7
4	1	35.7	36.0	33.7	34.6	0.8	2.7	5.9	4.0
	2	2.7	3.0	2.4	3.0	11.1	25.0	12.5	0.0
	3	8.3	8.9	8.0	8.6	7.2	7.5	3.8	3.5
	Weighted g/mi	0.369	0.386	0.343	0.373	4.6	8.7	7.6	3.5
5	1	37.5	38.7	35.7	37.0	3.2	3.6	5.0	4.6
	2	5.5	5.9	5.2	5.7	7.3	9.6	5.8	3.5
	3	22.2	22.4	21.6	21.7	0.9	0.5	2.8	3.2
	Weighted g/mi	0.589	0.610	0.561	0.585	3.6	4.3	5.0	4.3
6	1	30.1	31.4	28.1	29.4	4.3	4.6	7.1	6.8
	2	3.5	4.0	3.3	3.7	14.3	12.1	6.1	8.1
	3	7.6	8.0	7.4	7.6	5.3	2.7	2.7	5.3
	Weighted g/mi	0.345	0.368	0.323	0.346	6.7	7.1	6.8	6.4
7	1	50.5	50.0	48.0	49.9	-1.0	4.0	5.2	0.2
	2	7.5	8.4	7.4	8.2	12.0	10.8	1.4	2.4
	3	19.5	20.1	19.2	19.9	3.1	3.6	1.6	1.0
	Weighted g/mi	0.701	0.729	0.678	0.721	4.0	6.3	3.4	1.1
8	1	45.0	46.1	42.4	43.5	2.4	2.6	6.1	6.0
	2	3.9	4.7	3.6	4.4	20.5	22.2	8.3	6.8
	3	22.2	22.8	21.5	21.7	2.7	0.9	3.3	5.1
	Weighted g/mi	0.591	0.627	0.557	0.590	6.1	5.9	6.1	6.3
9	1	23.8	24.7	22.7	23.4	3.8	3.1	4.8	5.6
	2	4.8	5.4	4.4	4.9	12.5	11.4	9.1	10.2
	3	8.8	9.1	8.4	8.8	3.4	4.8	4.8	3.4
	Weighted g/mi	0.351	0.387	0.327	0.351	10.3	7.3	7.3	10.3
Summary									
Mean	1	38.6	39.2	36.4	37.6	1.8	3.3	6.0	4.5
	2	4.6	5.2	4.3	4.9	12.1	14.0	7.4	5.6
	3	12.8	13.2	12.4	12.8	3.9	4.3	3.6	3.2
	Weighted g/mi	0.483	0.507	0.454	0.484	5.3	6.7	6.6	5.3
Range	1	23.8 to 50.5	24.7 to 50.0	22.7 to 48.0	23.4 to 49.9	-1.0 to 4.3	2.6 to 4.6	4.8 to 7.1	0.2 to 6.8
	2	2.7 to 7.5	3.0 to 8.4	2.4 to 7.4	3.0 to 8.2	7.3 to 20.5	7.7 to 25.0	1.4 to 14.7	0.0 to 13.0
	3	6.2 to 22.2	6.6 to 22.8	5.8 to 21.6	6.3 to 21.7	0.9 to 7.2	0.5 to 8.6	1.6 to 6.9	0.0 to 5.3
	Weighted g/mi	0.345 to 0.701	0.368 to 0.729	0.323 to 0.678	0.346 to 0.721	2.8 to 10.3	4.3 to 8.9	3.4 to 10.3	1.1 to 10.3
95% Confidence Interval of Mean % Difference	1					0.4 to 3.2	2.8 to 3.8	5.4 to 6.6	3.0 to 6.0
	2					8.8 to 15.4	9.3 to 18.7	4.0 to 10.8	2.4 to 8.8
	3					2.3 to 5.5	2.1 to 6.5	2.4 to 4.8	1.8 to 4.6
	Weighted g/mi					3.5 to 7.1	5.6 to 7.8	5.2 to 8.0	3.2 to 7.4

several different blends of H_2/He mixed fuel. The analyzers were all spanned using a cylinder of 20.9% O_2 propane/air. The difference in measurement due to the reduced O_2 concentration of the 16.5% O_2 cylinder is listed below:

Percent H_2 of the H_2/He Fuel	Difference Due to O_2 Change From 20.9% to 16.5%
35	- 1%
40	- 2%
45	- 3%
60	- 6%
100	-16%

The measurement of propane/16.5% O_2/N_2 was significantly reduced using 60% H_2/He fuel. It is, therefore, possible that the expected increase in emission measurements was overwhelmed by an overall decrease in analyzer sensitivity due to the reduced O_2 background concentration in diluted exhaust bags.

ANALYZER PRECISION

Because the reduction of sample flow rate to the burner to improve relative response characteristics also results in a proportional decrease in sensitivity, several undesirable characteristics

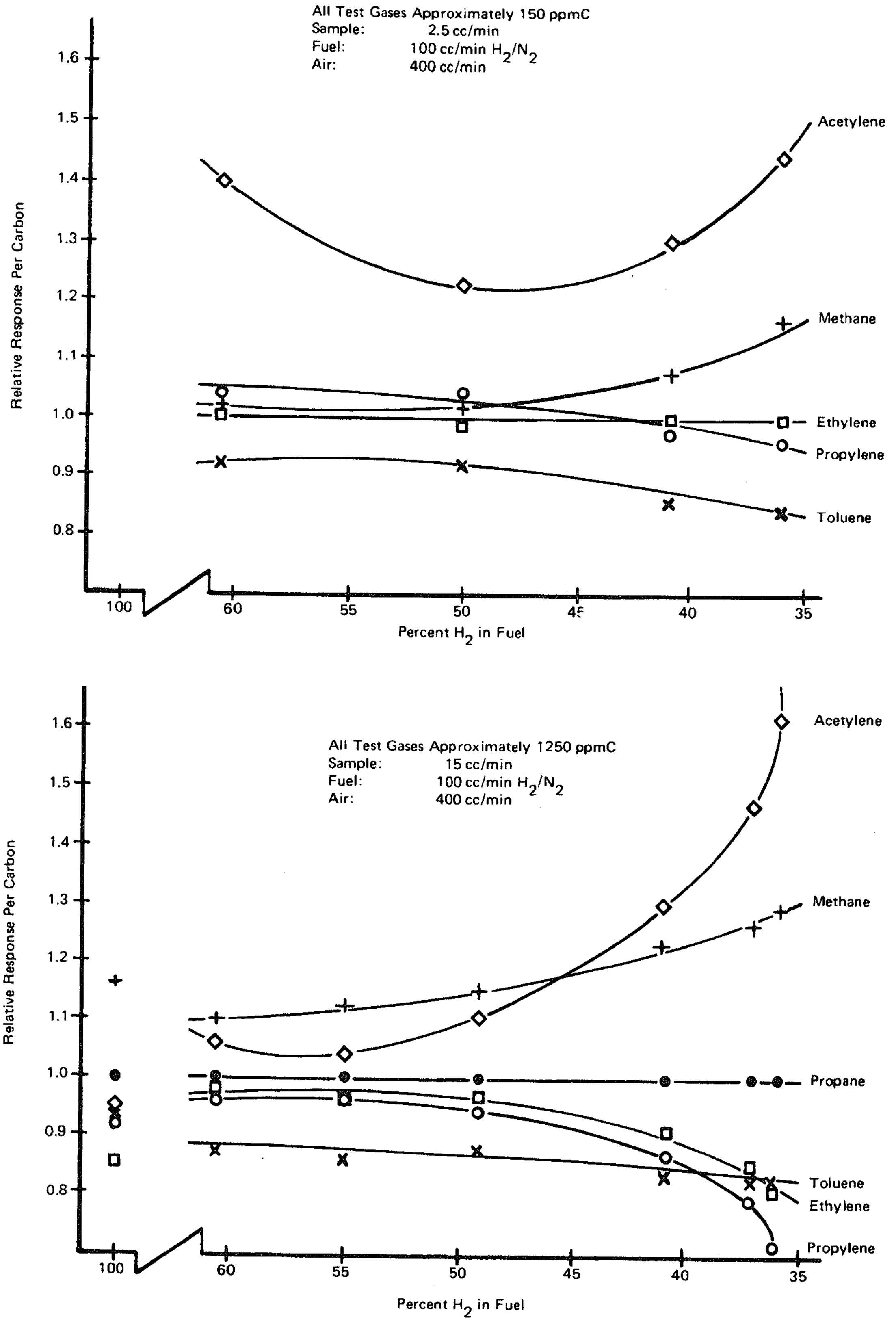

Fig. 10 - Effect of fuel composition on relative response - fuel diluent - N_2

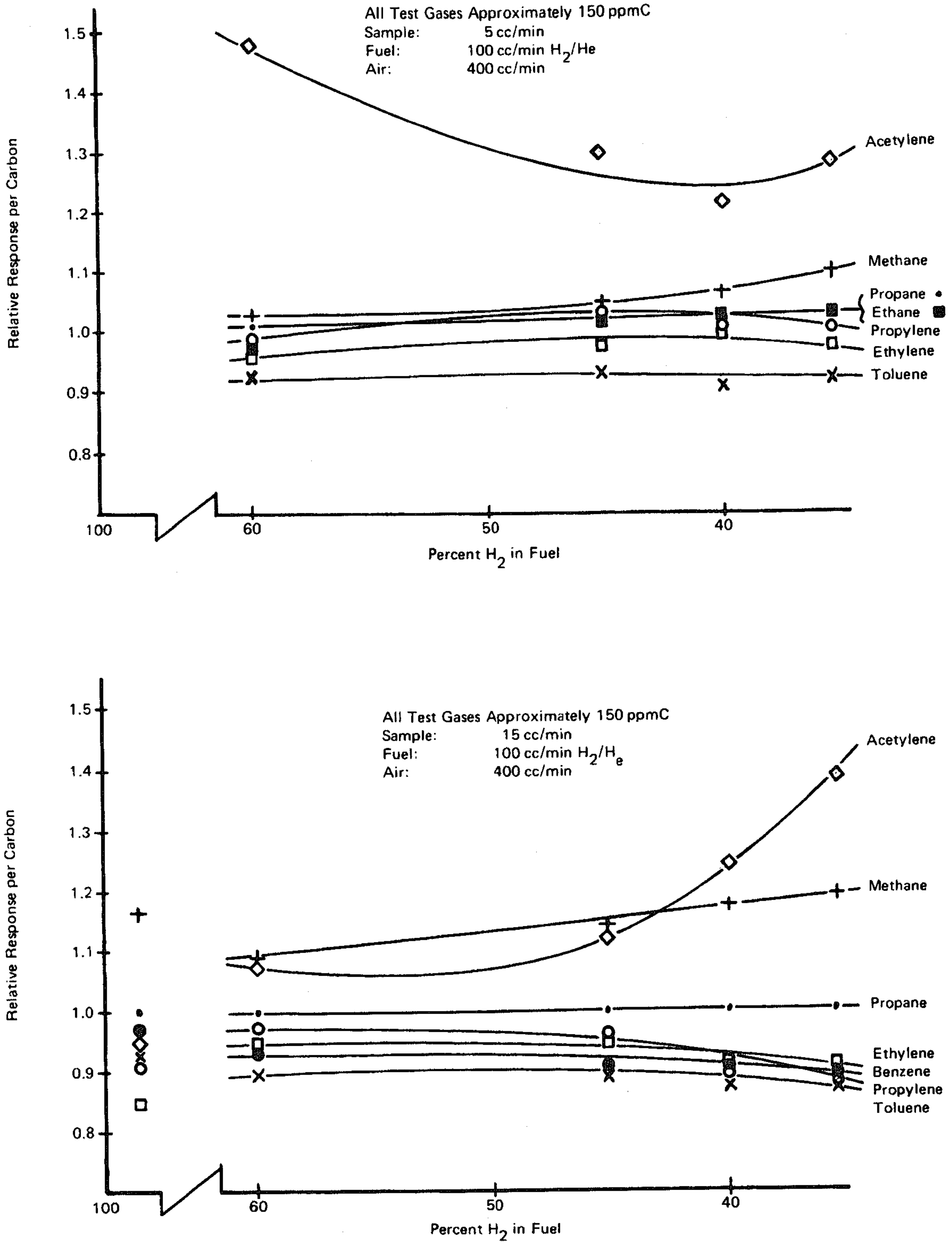

Fig. 11 - Effect of fuel composition on relative response - fuel diluent - He

can become critical. These include decreases in signal to noise ratio, loss of precision, and increased sensitivity to by-pass flow rate. To determine the extent that sample flow rate could be decreased before any undesirable characteristics became significant, these characteristics were measured at several sample pressure settings.

Two analyzers were calibrated for 0 to 300 ppmC (0 to 100 ppm propane) full scale at a

Table V - Effect of Fuel Composition on the Measurement of Dilute Exhaust Bags

Analyzer	B1	B2	B3
Fuel H_2 Concentration	40%	60%	100%
Fuel He Concentration	60%	40%	-
Fuel Flow Rate (cc/min)	100	100	100
Sample Flow Rate (cc/min)	15	15	15
Air Flow Rate (cc/min)	400	400	400

		Analyzer Measurement (ppm)			Percent Difference in Measurement Compared to 40% H_2	
Vehicle	Phase	40% H_2	60% H_2	100% H_2	60% H_2	100% H_2
1	1	41.5	39.8	38.5	- 4.1	- 7.2
	2	3.0	3.8	4.5	26.7	50.0
	3	6.8	6.7	6.6	- 1.5	- 2.9
	Weighted g/mi	0.454	0.465	0.476	2.4	4.9
2	1	41.8	40.5	39.8	- 3.1	- 4.8
	2	3.4	2.7	2.5	-20.6	-26.5
	3	7.9	7.2	6.6	- 8.9	-16.5
	Weighted g/mi	0.479	0.442	0.425	- 7.7	-11.3
3	1	68.9	66.4	63.7	- 3.6	- 7.6
	2	25.3	24.0	24.0	- 5.1	- 5.1
	3	37.0	35.6	34.4	- 3.8	- 7.0
	Weighted g/mi	1.610	1.540	1.510	- 4.4	- 6.2
4	1	29.4	28.6	27.6	- 2.7	- 6.1
	2	3.6	3.4	2.9	- 5.6	-19.4
	3	6.8	6.0	6.0	-11.8	-11.8
	Weighted g/mi	0.385	0.366	0.343	- 4.9	-10.9
5	1	7.4	6.8	7.2	- 8.1	- 2.7
	2	3.3	3.0	3.6	- 9.1	9.1
	3	14.1	13.6	13.4	- 3.6	- 5.0
	Weighted g/mi	0.287	0.270	0.288	- 5.9	0.3
6	1	64.5	61.5	59.5	- 4.7	- 7.8
	2	5.2	6.6	6.8	26.9	30.8
	3	10.3	9.6	9.4	- 6.8	- 8.7
	Weighted g/mi	0.719	0.733	0.723	1.9	0.6
7	1	41.8	41.0	40.2	- 1.9	- 3.8
	2	8.4	7.2	7.8	-14.3	- 7.1
	3	31.6	30.4	30.4	- 3.8	- 3.8
	Weighted g/mi	0.856	0.803	0.815	- 6.2	- 4.8
8	1	46.4	45.0	44.2	- 3.0	- 4.7
	2	4.0	3.5	3.5	-12.5	-12.5
	3	8.9	8.0	8.1	-10.1	- 9.0
	Weighted g/mi	0.540	0.506	0.501	- 6.3	- 7.2
Summary						
Mean	1	42.7	41.2	40.1	- 3.9	- 5.6
	2	7.0	6.8	7.0	- 1.7	- 2.4
	3	15.4	14.6	14.4	- 6.3	- 8.1
	Weighted g/mi	0.666	0.641	0.635	- 3.9	- 4.3
Range	1	7.4 to 68.9	6.8 to 66.4	7.2 to 63.7	-8.1 to -1.9	-7.8 to -2.7
	2	3.0 to 25.3	2.7 to 24.0	2.5 to 24.0	-20.6 to 26.9	-26.5 to 50.0
	3	6.8 to 37.0	6.0 to 35.6	6.6 to 34.4	-11.8 to -1.5	-16.5 to -2.9
	Weighted g/mi				-7.7 to 2.4	-11.3 to 4.9
95% Confidence Interval of Mean Percent Change	1				-5.0 to -2.8	-7.1 to -4.1
	2				-16.6 to 13.2	-23.7 to 18.9
	3				-9.3 to -3.3	-11.7 to -4.5
	Weighted g/mi				-7.1 to -0.7	-8.9 to +0.3

common sample pressure setting. At each sample pressure setting, the following measurements were taken:

1. Peak-to-peak noise at both zero and span (250 ppmC propane/air) was measured using a strip chart recorder.
2. Precision was measured as the standard deviation of ten repetitive readings of zero and span gas expressed as a percentage of full scale.
3. Sensitivity to by-pass flow rate was measured as the percent change in the

readings of the span gas as by-pass flow rate was increased or decreased in one scfh increments from the standard five scfh flow.

The results of the above testing are reported below:

Sample Pressure (psig)	Approximate Flow Rate (cc/min)	Peak-to-Peak Noise (%FS)		Precision (%FS)		Sensitivity to Bypass Flow Rate (Percent change in reading for each scfh change in flow)
		Zero	Span	Zero	Span	
5	25	0.1	0.1	0.03	0.06	0.1
3	15	0.1	0.1	0.03	0.05	0.2
2	10	0.1	0.1	0.03	0.14	0.5
1	5	0.1	0.2	0.03	0.24	2.1
0.5	2	0.1	0.2	0.03	0.28	10 to 20

Note that below one psig sample pressure, the sensitivity to by-pass flow rate becomes very critical with 10% to 20% changes in reading for each one scfh change. This indicates operation of the pressure regulator outside of its usable limits. Also, at low flow rates, precision of the analyzer at span is becoming significantly large (0.28% FS or 0.8 ppmC). It becomes apparent that the minimum sample pressure used on the Beckman Model 400 analyzer should be one psig, which corresponds to approximately five cc/min sample flow.

SUMMARY

Investigation of instrument-to-instrument correlation of the FID hydrocarbon analyzer showed that although the analyzers had been peaked* with the sample pressure set at 3 psig, the corresponding flow rates of sample, fuel, and air were not the same for each instrument. Correlation was improved by actually setting the same sample, fuel, and air flow rates for each instrument. With the improved procedure, the instrument-to-instrument variance of the measurements of several gases containing different individual hydrocarbons was reduced by a factor of two. This reduction in variance was shown to be statistically significant at the 95% confidence level. The variance of the measurements of dilute exhaust samples from test vehicles was reduced, but could not be shown to be statistically significant due to the small sample size.

The relative response of the FID to various hydrocarbon types (in air) was dependent on sample, fuel, and air flow rates, fuel type, and fuel composition. Sample and fuel flow rates had the most effect. Air flow rate, once it was above some minimum value (approximately four times the fuel flow rate), had little effect on relative response.

Reducing sample flow rate substantially improved the uniformity of response. Because of the associated loss in sensitivity and inherent pressure control problems of the sample back-pressure regulator, the minimum maintainable sample flow rate was approximately 5 cc/min. Increasing fuel flow rate also improved the uniformity of response, but not to the same degree that reducing the sample flow rate did. At any set of flow parameters, 40% hydrogen in helium (H_2/He) burner fuel gave slightly better relative response than did 40% hydrogen in nitrogen (H_2/N_2) fuel.

Flow rates and fuel type influenced the measurement of vehicle emissions, as well as pure gases. Dilute exhaust sample bags from the 1975 emission tests of nine 1975 vehicles were measured by analyzers using different sample flow rates and fuel types. From these bag measurements, the weighted hydrocarbon emission levels, in g/mi, were computed. The average change in emissions in g/mi is listed below:

Change in FID Condition	Average Change in Measured g/mi Emission
Change from 16 cc/min. to 2.5 cc/min. sample flow rate using H_2/N_2 fuel.	+6.6%
Same as above using H_2/He fuel	+5.3%
Change from H_2/N_2 to H_2/He fuel at 2.5 cc/min. sample flow rate	+5.3%
Same as above at 16 cc/min. sample flow rate	+6.7%

Changes in FID conditions which tended to improve uniformity of response, tended to raise exhaust emission measurements.

Mixed fuels with H_2 between 50% and 60% in either N_2 or He showed improved relative response over fuels of the standard composition of 40% H_2. As fuel composition was reduced below 40% H_2, response became more non-uniform at an ever-increasing rate. Between 30% and 35% H_2, the flame became so lean it would not remain lit.

Although response characteristics were better using 50% to 60% H_2 fuels, there were some corresponding increase in sensitivity to varying O_2 concentration of the sample (O_2 effects). The reduction in the measurement of a cylinder of 58 ppm propane/16.5% O_2/N_2, compared to the 60 ppm propane/20.9% O_2/N_2 span gas was 2% using 40% H_2/He fuel and 6% using 60% H_2/He fuel. Since the O_2 content of dilute exhaust bags does vary slightly from the span gas (18% compared to 20%), increased sensitivity to O_2 effects must be weighed against the improved relative response of 50% to 60% H_2 fuels.

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* A process by which fuel and air flow rates are adjusted for maximum analyzer sensitivity to the calibration gas.

RECOMMENDATIONS

As a result of this investigation, the following steps are recommended for optimization of the Beckman Model 400 FID for analysis of dilute exhaust sample bags from the Federal Vehicle Emission Test. Steps are listed in decreasing order of importance.

1. Maintain sample flow rate at a minimum (suggested flow rate: 5 cc/min).
2. Use H_2/He mixed fuel (suggested composition: 40% H_2).
3. Use high fuel flow rate to the FID burner (suggested flow rate: 100 - 120 cc/min.).
4. Use high air flow rate to the FID burner (suggested flow rate: four times the fuel flow rate).

No matter what flow parameters are used, it is important to set the burner flow rates of each instrument to the same value to obtain good correlation between instruments.

Although the above steps are recommended specifically for analyzers being used for analysis of dilute exhaust sample bags, they can be applied to FID's in other applications providing relative response optimization is considered in light of the expected oxygen level of the sample, the response time needed, and the sensitivity required.

DISCUSSION

From the data presented in this report, it can be concluded that burner flow parameters and fuel type determine, to a large extent, the relative response characteristics of the Beckman 400 FID. Uniformity of reponse is improved by the use of low sample flow rates, high fuel and air flow rates, H_2/He mixed fuel, and fuel compositions somewhat higher than 40% H_2.

If the relative response of the FID is uniform, accurate measurements of the complex hydrocarbon mixtures found in exhaust samples are possible. If the relative response of the FID is non-uniform, two major factors will determine the direction and magnitude of error in the measurement of exhaust hydrocarbons. One factor is the degree of non-uniformity of the response characteristics of the FID: the more non-uniform, the more error that is possible. The other factor is the composition of the exhaust hydrocarbon sample being measured.

Assume that the responses to the hydrocarbons not specifically measured in this study are similar to other hydrocarbons of the same family that were measured. This is a reasonable assumption based on the studies of other investigators. (1, 2) When spanned on propane, a Beckman Model 400 FID having non-uniform response characteristics will measure acetylene high, methane high, other paraffins correctly, and olefins and aromatics low. If the sample contains a majority of olefins and aromatics, it will tend to measure lower than true. The greater the percentage of paraffins (which tend to be measured correctly) the less the percentage of acetylene, methane, olefins and aromatics to contribute to error. Since in actual car exhaust the ratios between acetylene, methane, olefins, aromatics, and paraffins can vary considerably from car to car, the direction and magnitude of the error in measurement by a FID with non-uniform response will also vary. In general, though, most emissions from non-catalyst vehicles tend to be olefinic/aromatic in nature, (5) while emissions from catalyst vehicles tend to be less olefinic/aromatic in nature with an increased amount of methane. Therefore, one might predict that measurement of exhaust emissions from non-catalyst vehicles by a FID with non-uniform response will tend to be lower than actual. However, with catalyst vehicles, the increase in methane closely offsets the olefins and aromatics making the direction of error unpredictable. Actual measurements of dilute catalyst vehicle exhaust performed in this study showed higher measurements as response became more uniform. This suggests that catalyst vehicle exhaust is still slightly olefinic/aromatic in nature.

As mentioned in the Theory section, non-uniform response arises from two competing mechanisms that occur when internal oxygen is introduced into the flame with the sample. Some hydrocarbons are more readily oxidized by this internal oxygen, producing responses that do not fully participate in the FID ionization raction. At the same time, internal oxygen increases the oxygen atom concentration within the flame which tends to increase overall sensitivity. Possibly, reduced sample flow or increased fuel flow both serve to reduce the concentration of this internal oxygen which reduces the rate of these two mechanisms.

F.M. Black, el. al. (6) have recently reported several similar relative response characteristics for two other Beckman analyzers; the Model 108 and the Model 402. Our own experience with the Horiba Model FIA-21 FID and the IPM Model RS-5M FID has also shown relative response characteristics somewhat similar to those of the Beckman 400 FID. This suggests that possibly all FID's have similar relative response characteristics and can, therefore, be optimized using procedures developed herein for the Beckman 400 FID.

As the concentration of internal oxygen is also dependent upon the amount of oxygen in the sample, analyzers measuring samples having little or no oxygen will have more uniform relative response characteristics during those measurements than they will during measurements of samples in air. This means that FID's measuring raw vehicle exhaust, for example, need not have major emphasis placed on optimization of relative response characteristics, although it should still be considered.

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